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Multi-coated $YBa_2Cu_3O_{7-x}$ Films Fabricated by a Fluorine-Free Sol-Gel Process

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$YBa_2C_3O_{7-x}$ films were fabricated on a $SrTiO_3$ (100) substrate using a trimethylaceate propionic acid (TMAP)-based MOD process by controlling the precursor solution viscosity, firing temperature, and by using various coatings. The viscosity of the precursor solution was controlled by the addition of Xylenes. The films were heat treated with different temperatures from 750 to 800°C. c-axis oriented films were obtained. After adding 9 ml of Xylene into the precursor solution, the T_c of the YBCO film, which was coated 2 times and heat treated at 800°C, was 86 K and the measured J_c was above 2.5 MA/cm^2 at 77 K in a zero-field.

Keywords : YBCO coated conductor, fluorine-free process, xylene, multi-coating

1. Introduction

Biaxially textured $YBa_2C_3O_{7-x}$ (YBCO) coated conductors are very promising for various applications, for example, superconducting motors, cables, transformers, and generators [1]. A YBCO film was fabricated using various techniques, for instance, pulsed laser deposition (PLD), metal-organic chemical vapor deposition (MOCVD), an e-beam process, metal organic deposition (MOD), etc [2]. Among them, the MOD process is considered to be one of the most promising methods due to its relatively simple and low-cost process for long length scale production of YBCO-coated conductors. The MOD process has the coating of a metal-organic precursor solution on a substrate, and then thermal decomposition is followed to form the final desired compound. Generally the MOD processes are characterized in terms of different chemical sources used in the process, such as trifluoroacetate (TFA) MOD and fluorine-free MOD. The conventional TFA-MOD process using metal-TFA salts in a precursor solution generates a large amount of HF gas during the pyrolysis step, which is severely corrosive to the precursor films. Therefore, it was difficult to obtain dense and crack-free films by a routine process and moreover the thickness of precursor films is limited to low values after single coating and pyrolysis [3]. To overcome these problems, a number of studies have been carried out and recently the fluorine-free sol-gel method, like the TMAP-MOD process, has been developed and optimized. For the fluorine-free sol-gel process, metal acetylacetonates, metal naphthenates, metal trimethylacetates, metal citrates, and metal-acetate have been selected as precursors by some groups [4-9].

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The film deposited using the TMAP-MOD process consequently does not generate fluorine-containing compounds, including BaF_2 and HF, and results in a much denser microstructure than films prepared by the TFA-MOD process [10-13]. The highest current densities of the film by the TMAP process exceed 1.6×10^6 A/cm^2 [14]. Whereas the primary disadvantage of the TMAP-MOD is that the precursor layer is very thin, and the current density drops dramatically as the thickness increases [15].

The overall objective of this research is to examine and evaluate the influence of multiple coatings on the structural and electrical characteristics of YBCO film by applying the TMAP-MOD technique. For multiple coatings, the Xylene content in the precursor solution plays a critical role in the viscosity and wettability in a solution. In this paper, we will systematically evaluate the effect of Xylene on the film morphology and electrical properties in detail.

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2. Experimental

The YBCO films were deposited on $SrTiO_3$ (100) using the TMAP-MOD method. $Y(NO_3)_3$ and $Cu(NO_3)_2$ were used as the starting materials with $NH_4(C_4H_9COO)$ as the main solvent. Initially, $Y(NO_3)_3$ and $Cu(NO_3)_2$ were dissolved in different $NH_4(C_4H_9COO)$ solutions at room temperature in order to obtain $Y(C_4H_9COO)_3$ [Y-trimethylacetate] and $Cu(C_4H_9COO)_2$ [Cu-trimethylacetate], respectively. $Y(C_4H_9COO)_3$ and $Cu(C_4H_9COO)_2$ were dried at 70 °C. Finally $Y(C_4H_9COO)_3$, $Ba(OH)_2$, and $Cu(C_4H_9COO)_2$ were dissolved in 8 ml propionic acid with a molar ratio of Y:Ba:Cu = 1:2:3 and heated at 80 °C for 5 hour. Afterwards, 2 ml of amine was added to increase the solubility. Solution viscosity was adjusted by the addition of Xylene. The viscosity of the precursor solution slowly decreased as the amount of Xylene increased from 0 to 9 ml. After filtration, the precursor solution was deposited onto the $SrTiO_3$ (100) substrate by a spin-coater at a speed of 3000-4000 rpm for 30 seconds. The coated films were baked at 200 °C for 5 minute. The film thickness was controlled by repeating the spin-coating and baked process up to 3 times under the same condition. Baked films were subjected to calcination in wet nitrogen gas mixed with 200 ppm oxygen (dew point of 25 °C) at 400 °C for 10 hour. Calcined films were fired at 750, 775, and 800 °C for 1.5 hour. Finally the temperature was cooled down to 450 °C for 30 minute under dry nitrogen gas mixed with 200 ppm oxygen. The film thickness after 1, 2, and 3 coatings was 198 nm, 329 nm, and 424 nm, respectively. For the structure and phase identification, an X-ray diffractometer (XRD) with Cu Kα radiation was used. Surface and cross-sectional morphologies were observed using field emission scanning electron microscopy (FE-SEM). Critical transition temperatures (T_c) and critical current densities (J_c) were measured using a magnetic property measurement system (MPMS).

3. Result and Discussion

Fig. 1 shows the DT-TGA result for the YBCO precursor solution derived with 9 ml of Xylene additive. As seen in Fig. 1, most evaporation was occurred between 150 °C to 250 °C and the overall decomposition of more than 80% was completed until 500 °C. It was known that the decomposition temperature of copper trimethylacetate is 200-250 °C, that of yttrium trimethylacetate is 200-520 °C [16], and that of barium hydroxide is 490 °C [17]. However, the barium hydroxide possibly reacted with propionic acid to form a new material by a neutralization reaction during gel formation.

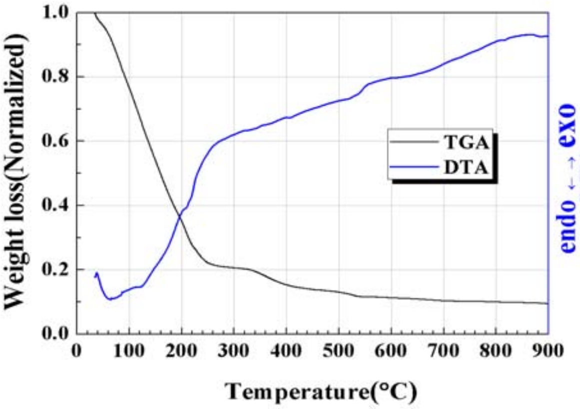


Fig. 1. DT-TGA analysis for YBCO precursor solution derived from 9 ml Xylene additive.

Fig. 2 shows the cross-sectional and surface morphology of the film fired at 750 °C in terms of different amount of Xylene from 0 to 9 ml. It was found that the viscosity of the precursor solution has a tendency to decrease from 153, 130, 102, 76, and to 55 cP, as the amounts of Xylene increases from 0 to 9 ml in the precursor solution. Also the film thickness decreased from 641, 398, 441, 401, and to 186 nm with the addition of Xylene. As shown in Fig. 2, the film surface became dense as the Xylene amount increased. It was known that a dense surface morphology plays a critical role in achieving high critical currents and therefore a porous film limits the current transport properties [18, 19].

Fig. 3 shows the X-ray diffraction patterns of the YBCO films for different amount of Xylene in precursor solution. The diffraction patterns observed in Fig. 3 indicate that the YBCO (00*l*) peak intensities slightly increased as the Xylene amount increased and the YBCO film prepared with 9 ml Xylene has the strongest peak intensity. When over 9 ml of xylene was added, YBCO was minimally deposited on the STO substrate because of the low viscosity below 30 cP. Based on this observation, 9 ml of Xylene added precursor solution has the most appropriate viscosity and wettability because this YBCO film had a dense surface morphology and strong peak intensities in XRD patterns, as compared with any other films added with different amounts of Xylene.

Fig. 4 shows the cross-sectional and surface morphology of 9 ml-added YBCO films that were heat treated from 755 to 800 °C after calcining at 400 °C. Fig. 4 suggests that the film thicknesses of the samples that were heat treated at 755 °C and 800 °C were 312 nm and 198 nm, respectively. The film that was heat treated at 800 °C exhibited a dense and smooth surface with a few round phases, while a porous and rough morphology was

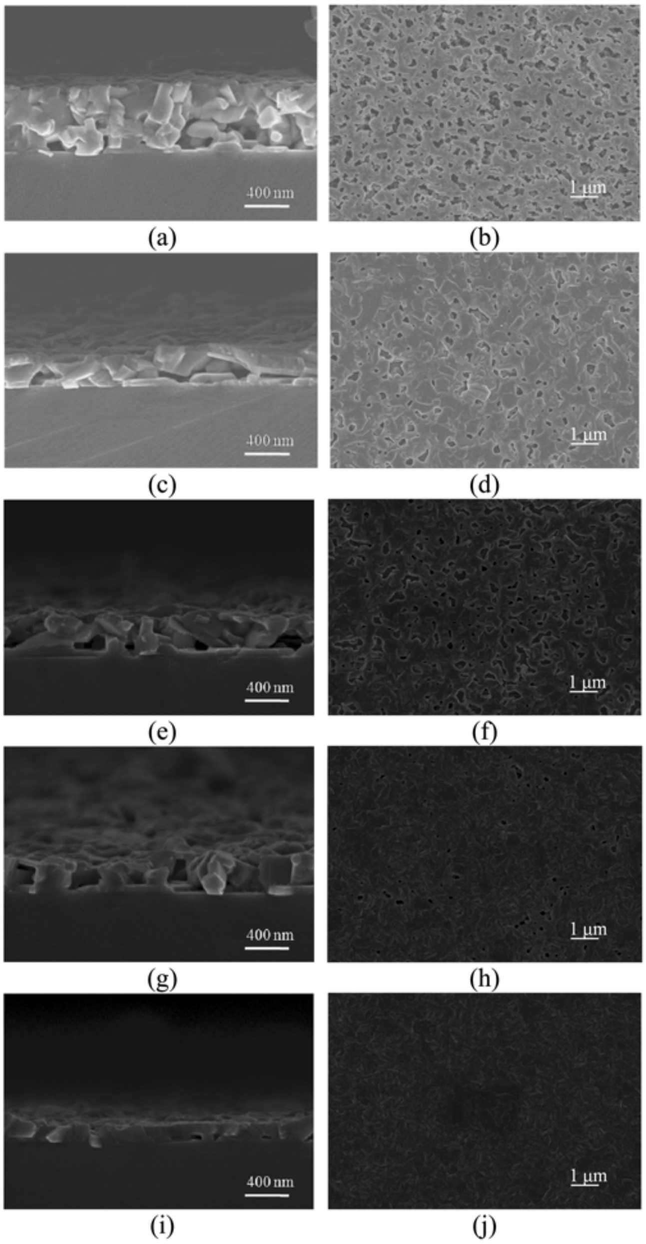


Fig. 2. The cross-sectional and surface morphologies of YBCO films fired at 750 ºC in terms of different amount of Xylene; [(a) and (b)]: 0 ml, [(c) and (d)]: 3 ml, [(e) and (f)] : 5 ml, [(g) and (h)]: 7, ml and [(i) and (j)]: 9 ml.

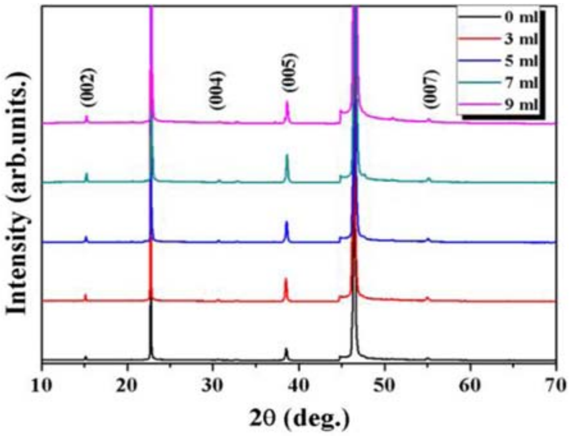


Fig. 3. The XRD diffraction patterns of the YBCO films derived from 0 to 9 ml of Xylene additive.

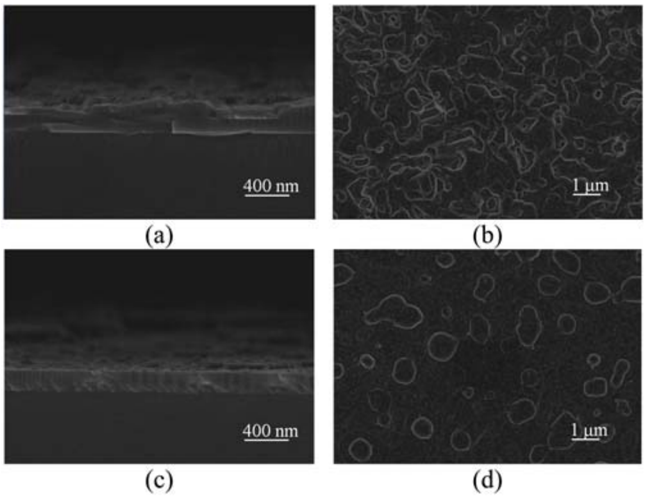


Fig. 4. Shows the cross-sectional and surface morphology of 9 ml-added YBCO films that were heat treated from 755 to 800 ºC after calcining at 400 ºC; [(a), (b)]: 755 ºC, and [(c), (d)] 800 ºC.

observed in the film that was heat treated at 755 ºC. It was known that the round phases are YBCO phases that were formed during the conversion process [20]. We believe that better surface morphologies of films heat treated at 800 ºC may be the reason for the achievement of high critical current densities in the magnetic field.

Fig. 5 represents X-ray diffraction θ-2θ patterns of 9 ml Xylene-added YBCO films heat treated from 750 to 800 ºC after calcining at 400 ºC. The XRD patterns shown in Fig. 5 indicate the film heat treated at 800 ºC exhibits c-axis oriented YBCO (00*l*) peaks with a high intensity and there is no second phase. Generally, it is seen that the peak intensity of YBCO (00*l*) increases with increasing heat treatment temperature.

Fig. 6 reveals the cross-sectional and surface morphology of multi-coated YBCO films. The thicknesses of YBCO films coated 2 and 3 times were 329 and 424 nm, respectively. The SEM images reveal that the surface agglomeration of the round phase formed during solidification increases with the number of coatings.

X-ray diffraction θ-2θ patterns of multi-coated YBCO films fabricated with 9 ml of Xylene precursor solution and heat treated at 800 ºC are shown in Fig. 7(a). All of the 1-, 2-, and 3-coated films have a c-orientation with

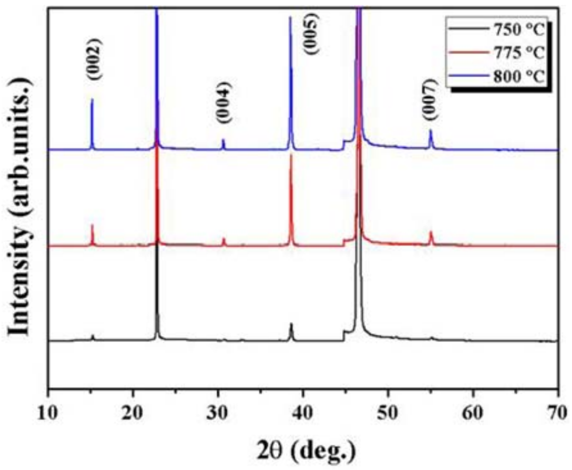
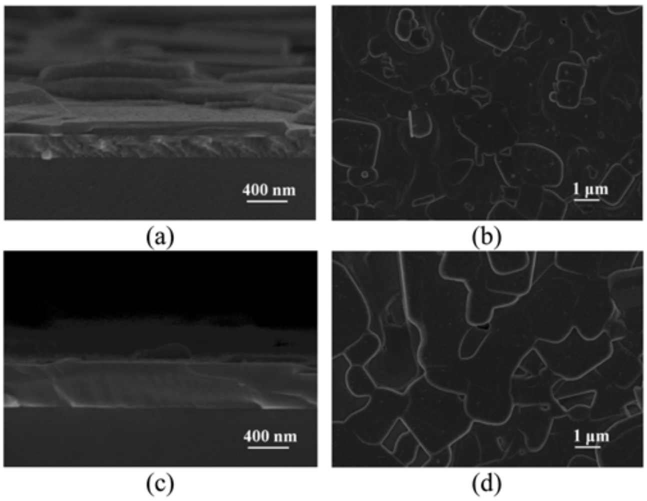


Fig. 5. The XRD patterns of the YBCO films fired at different temperatures after calcining at 400 °C.



(a) (b)

(c) (d)

Fig. 6. The SEM images of multi-coated YBCO films that were given 9 ml of Xylene and heat treated at 800 °C; (a), (b) 2-coated, and (c), (d) 3-coated.

high-intensity (00*l*) peaks, although a low-intensity peak corresponding to the randomly-oriented (112) plane are observed in the 3-coated film. Moreover, the peak intensity of YBCO (00*l*) generally increases with the number of coatings. The formation of randomly oriented grains is probably due to surface agglomeration. The highly textured YBCO films are also confirmed by X-ray ω-scans shown in Fig. 7(b). Based on X-ray ω-scans, the estimated full-width-half-maximum (FWHM), Δω, of 1-, 2- and 3-coated films was 0.16°, 0.14°, and 0.17°, respectively. YBCO (005) ω scan in the 2-coated film had the lowest FWMH of 0.14°, indicating a best out-of-plane.

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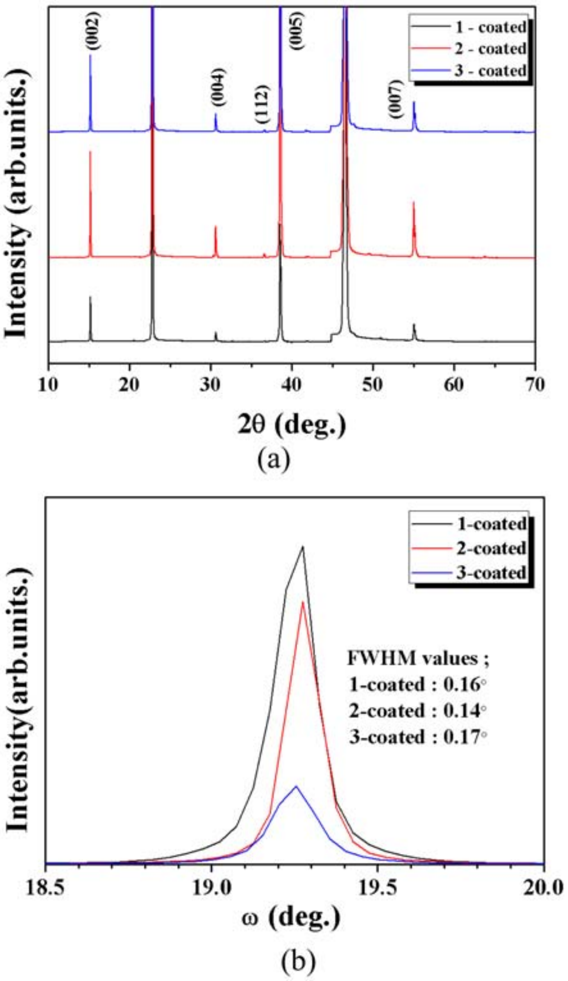
Fig. 8 shows critical temperatures, T_c, of multi-coated



(a)

(b)

Fig. 7. X-ray diffraction θ-2θ patterns of multi-coated YBCO films prepared with 9 ml of Xylene and heat treated at 800 °C; (a) XRD θ-2θ scan and (b) YBCO (005) ω-scan, the FWMH values are shown inside the patterns.

YBCO films. T_c (onset) values of 1-, 2-, and 3-coated YBCO films are 89 K, 89.5 K, and 87 K, respectively.

Fig. 9 demonstrates the critical current density, J_c, of multi-coated YBCO films at different temperatures with a magnetic field parallel to the c-axis. As seen in Fig. 9(a), the measured J_c of the 2-coated YBCO film was 2.5 MA/cm^2 at 77 K and a self-field, which is more than 1.3 MA/cm^2 more than the 1-coated film. However, the J_c of 3-coated YBCO film decreased drastically to 0.03 MA/cm^2, which is the lowest J_c value, as compared with the other two-coated films. This result indicates that the optimum coating times for maximizing the J_c value range was two times. Especially, the J_c value decreased systematically as the magnetic field increased in 1-, 2-, and 3-coated films. While J_c values in a high field region reflects flux pinning, while effective pinning centers in a high field region do not seem to be introduced for these films. It can be

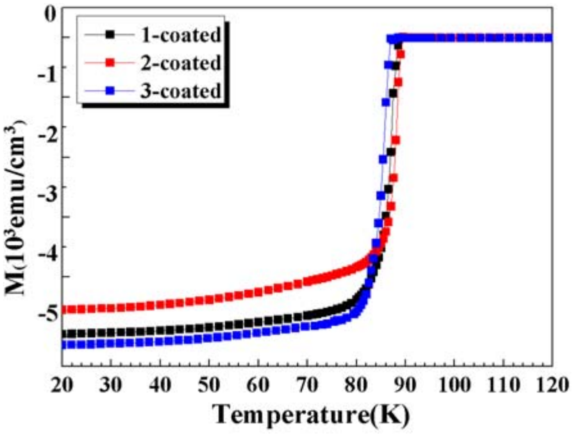


Fig. 8. Critical temperature, T_c, value of multi-coated YBCO films prepared with 9 ml of Xylene and heat treated at 800 °C.

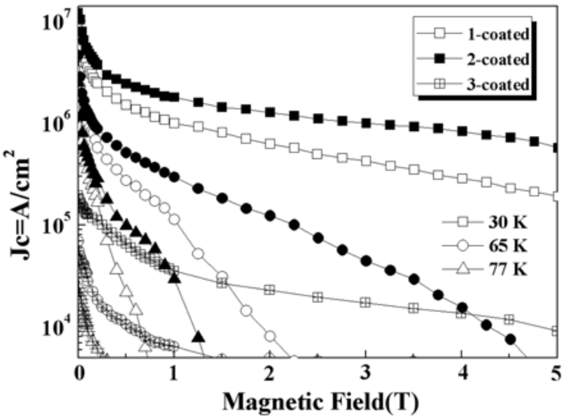


Fig. 9. Critical current density, J_c, versus magnetic field (30, 50, 65, 77 K, B//c) for YBCO films prepared with 9 ml of Xylene and heat treated at 800 °C.

concluded that the causes of the change in J_c may be associated with the YBCO (112) peak and surface agglomeration. The microstructure of the film remained uniform and then began to deteriorate after 2-time coating.

This result indicates that the optimum coating times for maximizing the J_c value range was two times.

5. Conclusion

We fabricated YBCO films on a $SrTiO_3$ (100) substrate with a TMAP-MOD process using TMAP solutions with different amounts of Xylene additive. The XRD and SEM results suggest that there are c-axis oriented YBCO films derived from all precursor solutions. As a result of this, the 9 ml Xylene added precursor solution has the most appropriate viscosity and wettability. The XRD and SEM results suggest that all the YBCO films derived from all precursor solutions are c-axis oriented. The 9 ml xylene-added precursor solution in our experiments has an optimal viscosity and wettability, and results in a highly dense YBCO film after heat treatment at 800 °C. T_c (onset) values of 1-, 2-, and 3-coated YBCO films are 89 K, 89.5 K, and 87 K, respectively. The highest J_c value of 2.5 MA/cm^2 at 77 K in a self-field is obtained from the 2-coated YBCO films derived from the 9 ml Xylene-added precursor solution that was heat treated at 800 °C.

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